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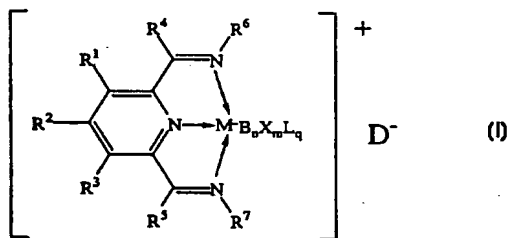
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C07F 15/00, 15/02, 15/06, 13/00, 9/00, 7/00, C08F 10/00, 4/64, 4/68, 4/695, 4/70		A1	(11) International Publication Number: WO 00/69869
			(43) International Publication Date: 23 November 2000 (23.11.00)
(21) International Application Number: PCT/GB00/01385		(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 12 April 2000 (12.04.00)			
(30) Priority Data: 9911245.0 15 May 1999 (15.05.99) GB			
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(54) Title: POLYMERISATION CATALYSTS



(57) Abstract

A complex is disclosed for the polymerisation of 1-olefins, having Formula (I) wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III], Ru[IV], V[II], V[III], V[IV], V[V], Ti[II], Ti[III] or Ti[IV]; and R¹ to R⁷ are each independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl or SiR'₃ where each R' is independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl; B is a chelating ligand comprising at least one atom from O, S, N and P bound directly to M; X is a monodentate monoanionic ligand; L is a ligand datively bonded to M; n is greater or equal to 1, m is greater or equal to 0 and q is greater or equal to 0, provided that n and m are integers or zero which satisfy the valency of the metal; and D is a compatible non-coordinating anion.

POLYMERISATION CATALYSTS

The present invention relates to transition metal complex compounds, to polymerisation catalysts based thereon and to their use in the polymerisation and copolymerisation of olefins.

The use of certain transition metal compounds to polymerise 1-olefins, for
5 example, ethylene, is well established in the prior art. The use of Ziegler-Natta catalysts, for example, those catalysts produced by activating titanium halides with organometallic compounds such as triethylaluminium, is fundamental to many commercial processes for manufacturing polyolefins. Over the last twenty or thirty years, advances in the technology have led to the development of Ziegler-Natta catalysts which have such high
10 activities that olefin polymers and copolymers containing very low concentrations of residual catalyst can be produced directly in commercial polymerisation processes. The quantities of residual catalyst remaining in the produced polymer are so small as to render unnecessary their separation and removal for most commercial applications. Such processes can be operated by polymerising the monomers in the gas phase, or in solution
15 or in suspension in a liquid hydrocarbon diluent. Polymerisation of the monomers can be carried out in the gas phase (the "gas phase process"), for example by fluidising under polymerisation conditions a bed comprising the target polyolefin powder and particles of the desired catalyst using a fluidising gas stream comprising the gaseous monomer. In the so-called "solution process" the (co)polymerisation is conducted by introducing the
20 monomer into a solution or suspension of the catalyst in a liquid hydrocarbon diluent under conditions of temperature and pressure such that the produced polyolefin forms as a solution in the hydrocarbon diluent. In the "slurry process" the temperature, pressure

and choice of diluent are such that the produced polymer forms as a suspension in the liquid hydrocarbon diluent. These processes are generally operated at relatively low pressures (for example 10-50 bar) and low temperature (for example 50 to 150°C).

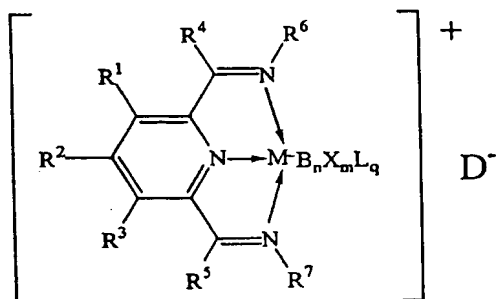
In recent years the use of certain metallocene catalysts (for example
5 biscyclopentadienylzirconiumdichloride activated with alumoxane) has provided catalysts with potentially high activity. However, metallocene catalysts of this type suffer from a number of disadvantages, for example, high sensitivity to impurities when used with commercially available monomers, diluents and process gas streams, the need to use large quantities of expensive alumoxanes to achieve high activity, and difficulties in
10 putting the catalyst on to a suitable support.

WO98/27124 discloses that ethylene may be polymerised by contacting it with certain iron or cobalt complexes of selected 2,6-pyridinecarboxaldehydebis(imines) and 2,6-diacetylpyridinebis(imines). Cationic versions of these complexes are disclosed, but only including monodentate anionic ligands into which ethylene can insert. WO
15 98/11144 discloses catalyst compositions comprising complexes of Group IVB, VB and VIII metals in which the ligands include chelating ligands where at least one atom from O, N, P or S is directly bound to the metal, plus a neutral Lewis base. However no permanent ligands of the type claimed below are disclosed. Our own copending application GB9903402.7 discloses certain vanadium and titanium complexes of selected
20 2,6-pyridinecarboxaldehydebis(imines) and 2,6-diacetylpyridinebis(imines), but only in the neutral form.

An object of the present invention is to provide a novel catalyst suitable for polymerising and oligomerising monomers, for example, olefins such as α -olefins containing from 2 to 20 carbon atoms, and especially for polymerising ethylene alone,
25 propylene alone, or for copolymerising ethylene or propylene with other 1-olefins such as C_{2-20} α -olefins. A further object of the invention is to provide an improved process for the polymerisation of olefins, especially of ethylene alone or the copolymerisation of ethylene or propylene with higher 1-olefins to provide homopolymers and copolymers having controllable molecular weights. For example, using the catalysts of the present
30 invention there can be made a wide variety of products such as, for example, liquid polyolefins, oligomers, linear α -olefins, branched α -olefins, resinous or tacky polyolefins, solid polyolefins suitable for making flexible film and solid polyolefins having high

stiffness.

In its first aspect, the present invention provides a complex having the Formula (I)



Formula (I)

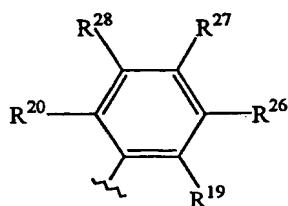
wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III], Ru[IV], V[II], V[III], V[IV], V[V], Ti[II], Ti[III] or Ti[IV]; and R¹ to R⁷ are each independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl or SiR'₃ where each R' is independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl;

B is a chelating ligand comprising at least one atom from O, S, N and P bound directly to M; X is a monodentate monoanionic ligand; L is a ligand datively bonded to M; n is greater or equal to 1, m is greater or equal to 0 and q is greater or equal to 0, provided that n and m are integers or zero which satisfy the valency of the metal; and D is a compatible non-coordinating anion.

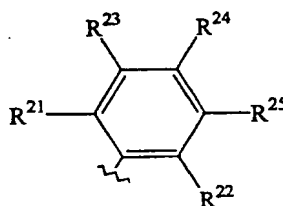
Preferably n = 1, m = 0 and q = 0 or 1.

R⁶ and R⁷ are preferably independently selected from substituted or unsubstituted alicyclic, heterocyclic or aromatic groups, for example, phenyl, 1-naphthyl, 2-naphthyl, 2-methylphenyl, 2-ethylphenyl, 2,6-diisopropylphenyl, 2,3-diisopropylphenyl, 2,4-diisopropylphenyl, 2,6-di-n-butylphenyl, 2,6-dimethylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2-t-butylphenyl, 2,6-diphenylphenyl, 2,4,6-trimethylphenyl, 2,6-trifluoromethylphenyl, 4-bromo-2,6-dimethylphenyl, 3,5 dichloro-2,6-diethylphenyl, and 2,6-bis(2,6-dimethylphenyl)phenyl, cyclohexyl and pyridinyl.

In a preferred embodiment R^6 is represented by the group "P" and R^7 is represented by the group "Q" as follows:



Group P



Group Q

wherein R^{19} to R^{28} are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more of R^1 to R^5 and R^{19} to R^{28} are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents.

The ring systems P and Q are preferably independently 2,6-hydrocarbylphenyl or fused-ring polyaromatic, for example, 1-naphthyl, 2-naphthyl, 1-phenanthrenyl and 8-quinolinyl. More preferably the ring systems P and Q are independently 2,4,6-hydrocarbylphenyl.

Preferably at least one of R^{19} , R^{20} , R^{21} and R^{22} is hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl. More preferably at least one of R^{19} and R^{20} , and at least one of R^{21} and R^{22} , is hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl. Most preferably R^{19} , R^{20} , R^{21} and R^{22} are all independently selected from hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl. R^{19} , R^{20} , R^{21} and R^{22} are preferably independently selected from methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, neopentyl, n-hexyl, 4-methylpentyl, n-octyl, phenyl and benzyl.

R^1 , R^2 , R^3 , R^4 , R^6 and R^{19} to R^{28} are preferably independently selected from hydrogen and C_1 to C_8 hydrocarbyl, for example, methyl, ethyl, n-propyl, n-butyl, t-butyl, n-hexyl, n-octyl, phenyl and benzyl.

In an alternative embodiment R^6 is a group having the formula $-NR^{29}R^{30}$ and R^7 is a group having the formula $-NR^{31}R^{32}$, wherein R^{29} to R^{32} are independently selected

from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more of R^1 to R^4 , R^6 and R^{29} to R^{32} are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents.

Illustrative but non-limiting examples of suitable ligands B are the following: β -diketonate, β -diketiminatate, dithioacetylacetonate, carboxylate, carbamate, thiocarboxylate, dithiocarboxylate, thiocarbamate, dithiocarbamate, xanthate, thioxanthate, phosphinate, thiophosphinate, dithiophosphinate, dialkyldithiophosphate, amidinate, bisimidazolate, phosphate, sulphurdiiminatate, amidate, tropolonate, oxalate, oxalate ester, nitrate, nitrite, carbonate, squarate, croconate, sulphinate, sulphate, sulphite, fluorosulphate, hydroxamate, thiohydroxamate, and dithiohydroxamate.

Particularly suitable ligands B are β -diketonates or β -diketiminatate, for example acetylacetonate or substituted acetylacetonates such as fluorinated derivatives.

The atom or group represented by X in the compounds of Formula (I) and (II) can be, for example, selected from selected from halide, hydride, hydrocarbyloxyde, carboxylate, hydrocarbyl, substituted hydrocarbyl and heterohydrocarbyl. Examples of such atoms or groups are chloride, bromide, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl, methoxide, ethoxide, isopropoxide, tosylate, triflate, formate, acetate, phenoxide and benzoate. Examples are for example, chloride, bromide; hydride; hydrocarbyloxyde, for example, methoxide, ethoxide, isopropoxide, phenoxide; carboxylate, for example, formate, acetate, benzoate; hydrocarbyl, for example, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl; substituted hydrocarbyl; heterohydrocarbyl; tosylate; and triflate. Preferably X is selected from halide, hydride and hydrocarbyl. Chloride is particularly preferred.

Illustrative but non-limiting examples of the ligand L are primary, secondary and tertiary amines, amides, phosphoramides, phosphines, phosphites, ethers, thioethers, nitriles, carbonyl compounds, for example, esters, ketones, aldehydes, carbon monoxide, carbon dioxide, sulphoxides, sulphones and boroxines.

Illustrative but non-limiting examples of the compatible, non-coordinating anion D are BF_4^- , SbF_6^- , PF_6^- and tetrakis(aryl)borates e.g. tetrakis(phenyl)borate and tetrakis(pentafluorophenyl)borate.

Preferably M is Fe, Co or V, particularly Fe.

Examples of complexes of the present invention include

- 2,6-diacetylpyridinebis(2,6-diisopropylanil)Fe(acetylacetonate)⁺ SbF₆⁻
- 2,6-diacetylpyridinebis(2-tert.-butylanil)Fe(acetylacetonate)⁺ SbF₆⁻
- 5 2,6-diacetylpyridinebis(2,3-dimethylanil)Fe(acetylacetonate)⁺ SbF₆⁻
- 2,6-diacetylpyridinebis(2-methylanil)Fe(acetylacetonate)⁺ SbF₆⁻
- 2,6-diacetylpyridinebis(2,4-dimethylanil)Fe(acetylacetonate)⁺ SbF₆⁻
- 2,6-diacetylpyridinebis(2,6-dimethylanil)Fe(acetylacetonate)⁺ SbF₆⁻
- 2,6-diacetylpyridinebis(2,4,6 trimethyl anil)Fe(acetylacetonate)⁺ SbF₆⁻
- 10 2,6-dialdiminepyridinebis(2,6-dimethylanil)Fe(acetylacetonate)⁺ SbF₆⁻
- 2,6-dialdiminepyridinebis(1-naphthil)Fe(acetylacetonate)⁺ SbF₆⁻ and
- 2,6-bis(1,1-diphenylhydrazone)pyridine.Fe(acetylacetonate)⁺ SbF₆⁻
- 2,6-diacetylpyridine(2,6-diisopropylanil)Co(acetylacetonate)⁺ SbF₆⁻
- 2,6-diacetylpyridinebis(2,6-diisopropylanil)Fe(hexafluoroacetylacetonate)⁺ SbF₆⁻
- 15 2,6-diacetylpyridinebis(2,4,6 trimethyl anil)Fe(hexafluoroacetylacetonate)⁺ SbF₆⁻
- 2,6-diacetylpyridinebis(2-methylanil)Fe(hexafluoroacetylacetonate)⁺ SbF₆⁻
- 2,6-diacetylpyridine(2,6-diisopropylanil)Co(hexafluoroacetylacetonate)⁺ SbF₆⁻
- 2,6-diacetylpyridinebis(2,6-diisopropylanil)Fe(acetylacetonate)⁺ B(C₆F₅)₄⁻
- 2,6-diacetylpyridinebis(2,4,6 trimethyl anil)Fe(acetylacetonate)⁺ B(C₆F₅)₄⁻
- 20 2,6-diacetylpyridinebis(2-methylanil)Fe(acetylacetonate)⁺ B(C₆F₅)₄⁻
- 2,6-diacetylpyridine(2,6-diisopropylanil)Co(acetylacetonate)⁺ B(C₆F₅)₄⁻
- 2,6-diacetylpyridinebis(2,6-diisopropylanil)Fe(hexafluoroacetylacetonate)⁺
B(C₆F₅)₄⁻
- 2,6-diacetylpyridinebis(2,4,6 trimethyl anil)Fe(hexafluoroacetylacetonate)⁺
- 25 B(C₆F₅)₄⁻
- 2,6-diacetylpyridinebis(2-methylanil)Fe(hexafluoroacetylacetonate)⁺ B(C₆F₅)₄⁻
- 2,6-diacetylpyridine(2,6-diisopropylanil)Co(hexafluoroacetylacetonate)⁺ B(C₆F₅)₄⁻

The present invention further provides a polymerisation catalyst comprising

- (1) a compound having the Formula (I) as hereinbefore defined, and
- 30 (2) an activating quantity of at least one activator compound.

The activator compound for the catalyst of the present invention is suitably selected from organoaluminium compounds and hydrocarbylboron compounds. Suitable

organoaluminium compounds include compounds of the formula AlR_3 , where each R is independently C_1 - C_{12} alkyl or halo. Examples include trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA), tri-n-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride, ethylaluminiumsesquichloride, methylaluminiumsesquichloride, and alumoxanes. Alumoxanes are well known in the art as typically the oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic or mixtures thereof. Commercially available alumoxanes are generally believed to be mixtures of linear and cyclic compounds. The cyclic alumoxanes can be represented by the formula $[\text{R}^{16}\text{AlO}]_s$, and the linear alumoxanes by the formula $\text{R}^{17}(\text{R}^{18}\text{AlO})_s$, wherein s is a number from about 2 to 50, and wherein R^{16} , R^{17} , and R^{18} represent hydrocarbyl groups, preferably C_1 to C_6 alkyl groups, for example methyl, ethyl or butyl groups. Alkylalumoxanes such as methylalumoxane (MAO) and trialkylaluminiums such as trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA) are preferred.

Mixtures of alkylalumoxanes and trialkylaluminium compounds are particularly preferred, such as MAO with TMA or TIBA. In this context it should be noted that the term "alkylalumoxane" as used in this specification includes alkylalumoxanes available commercially which may contain a proportion, typically about 10wt%, but optionally up to 50wt%, of the corresponding trialkylaluminium; for instance, commercial MAO usually contains approximately 10wt% trimethylaluminium (TMA), whilst commercial MMAO contains both TMA and TIBA. Quantities of alkylalumoxane quoted herein include such trialkylaluminium impurities, and accordingly quantities of trialkylaluminium compounds quoted herein are considered to comprise compounds of the formula AlR_3 additional to any AlR_3 compound incorporated within the alkylalumoxane when present.

Examples of suitable hydrocarbylboron compounds are boroxines, trimethylboron, triethylboron, dimethylphenylammoniumtetra(phenyl)borate, trityltetra(phenyl)borate, triphenylboron, dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl] borate, $\text{H}^+(\text{OEt}_2)[(\text{bis-3,5-trifluoromethyl)phenyl}]_4\text{borate}$, trityltetra(pentafluorophenyl)borate and tris(pentafluorophenyl) boron.

In the preparation of the catalysts of the present invention the quantity of activating compound selected from organoaluminium compounds and hydrocarbylboron compounds to be employed is easily determined by simple testing, for example, by the preparation of small test samples which can be used to polymerise small quantities of the monomer(s) and thus to determine the activity of the produced catalyst. It is generally found that the quantity employed is sufficient to provide 0.1 to 20,000 atoms, preferably 1 to 2000 atoms of aluminium or boron per atom of metal M in the compound of Formula (I).

It has been surprisingly found that the complexes of the present invention are easy to manufacture and can be handled in air. It has been shown that polymerisation catalysts can be prepared from neutral complexes of selected 2,6-pyridinecarboxaldehydebis(imines) and 2,6-diacylpyridinebis(imines) and an activator as disclosed in WO99/12981. The best catalyst activities have been generated with MAO as activator, because MAO is able to abstract a ligand to generate a cation and also alkylate the metal centre. However MAO is expensive, and cheaper activators are desirable. By preparing cationic complexes directly, as is disclosed in this invention, it is possible to achieve good catalyst activity from small quantities of a simple trialkylaluminium activator such as trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA), which can alkylate the metal centre.

The catalysts of the present invention can also include one or more other types of catalyst, such as those of the type used in conventional Ziegler-Natta catalyst systems, metallocene-based catalysts, monocyclopentadienyl- or constrained geometry based catalysts, or heat activated supported chromium oxide catalysts (eg Phillips-type catalyst).

The catalysts of the present invention can be unsupported or supported on a support material, for example, silica, alumina, $MgCl_2$ or zirconia, or on a polymer or prepolymer, for example polyethylene, polypropylene, polystyrene, or poly(aminostyrene).

If desired the catalysts can be formed in situ in the presence of the support material, or the support material can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. The catalysts of the present invention can if desired be supported on a heterogeneous catalyst, for example, a

magnesium halide supported Ziegler Natta catalyst, a Phillips type (chromium oxide) supported catalyst or a supported metallocene catalyst. Formation of the supported catalyst can be achieved for example by treating the transition metal compounds of the present invention with alumoxane or trialkylaluminium in a suitable inert diluent, for example a volatile hydrocarbon, slurrying a particulate support material with the product and evaporating the volatile diluent. The produced supported catalyst is preferably in the form of a free-flowing powder. The quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the transition metal compound.

Another method to prepare a supported catalyst is to slurry the transition metal compounds of the present invention in a suitable inert diluent, for example a volatile hydrocarbon, with a particulate support material and evaporating or filtering the volatile diluent. The produced supported catalyst is preferably in the form of a free-flowing powder. The quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the transition metal compound. This type of supported catalyst can be activated by trialkylaluminium activators in the polymerisation reactor or vessel. This type of process enables more controlled exotherms on catalyst injections into polymerisation reactors, and avoids agglomerate formation and sheeting in gas phase and slurry phase reactors.

The present invention further provides a process for the polymerisation and copolymerisation of 1-olefins, comprising contacting the monomeric olefin under polymerisation conditions with the polymerisation catalyst of the present invention. A preferred process comprises the steps of:

a) preparing a prepolymer-based catalyst by contacting one or more 1-olefins with a catalyst, and

b) contacting the prepolymer-based catalyst with one or more 1-olefins, wherein the catalyst is as defined above.

The polymerisation conditions can be, for example, solution phase, slurry phase, gas phase or bulk phase, with polymerisation temperatures ranging from -100°C to +300°C, and at pressures of atmospheric and above, particularly from 140 to 4100 kPa. If desired, the catalyst can be used to polymerise ethylene under high pressure/high temperature process conditions wherein the polymeric material forms as a melt in

supercritical ethylene. Preferably the polymerisation is conducted under gas phase fluidised bed or stirred bed conditions.

Suitable monomers for use in the polymerisation process of the present invention are, for example, ethylene and C₂₋₂₀ α -olefins, specifically propylene, 1-butene, 1-pentene, 1-hexene, 4-methylpentene-1, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, and 1-eicosene. Other monomers include methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene. Preferred monomers for homopolymerisation processes are ethylene and propylene.

The catalysts and process of the invention can also be used for copolymerising ethylene or propylene with each other or with other 1-olefins such as 1-butene, 1-hexene, 4-methylpentene-1, and octene, or with other monomeric materials, for example, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene.

Irrespective of the polymerization or copolymerization technique employed, polymerization or copolymerization is typically carried out under conditions that substantially exclude oxygen, water, and other materials that act as catalyst poisons. Also, polymerization or copolymerization can be carried out in the presence of additives to control polymer or copolymer molecular weights.

The use of hydrogen gas as a means of controlling the average molecular weight of the polymer or copolymer applies generally to the polymerisation process of the present invention. For example, hydrogen can be used to reduce the average molecular weight of polymers or copolymers prepared using gas phase, slurry phase, bulk phase or solution phase polymerisation conditions. The quantity of hydrogen gas to be employed to give the desired average molecular weight can be determined by simple "trial and error" polymerisation tests.

The polymerisation process of the present invention provides polymers and copolymers, especially ethylene polymers, at remarkably high productivity (based on the amount of polymer or copolymer produced per unit weight of complex employed in the catalyst system). This means that relatively very small quantities of transition metal complex are consumed in commercial processes using the process of the present invention. It also means that when the polymerisation process of the present invention is

operated under polymer recovery conditions that do not employ a catalyst separation step, thus leaving the catalyst, or residues thereof, in the polymer (e.g. as occurs in most commercial slurry and gas phase polymerisation processes), the amount of transition metal complex in the produced polymer can be very small.

- 5 Slurry phase polymerisation conditions or gas phase polymerisation conditions are particularly useful for the production of high or low density grades of polyethylene, and polypropylene. In these processes the polymerisation conditions can be batch, continuous or semi-continuous. Furthermore, one or more reactors may be used, e.g. from two to five reactors in series. Different reaction conditions, such as different
- 10 temperatures or hydrogen concentrations may be employed in the different reactors. In the slurry phase process and the gas phase process, the catalyst is generally metered and transferred into the polymerisation zone in the form of a particulate solid either as a dry powder (e.g. with an inert gas) or as a slurry. This solid can be, for example, a solid catalyst system formed from the one or more of complexes of the invention and an
- 15 activator with or without other types of catalysts, or can be the solid catalyst alone with or without other types of catalysts. In the latter situation, the activator can be fed to the polymerisation zone, for example as a solution, separately from or together with the solid catalyst. Preferably the catalyst system or the transition metal complex component of the catalyst system employed in the slurry polymerisation and gas phase polymerisation is
- 20 supported on one or more support materials. Most preferably the catalyst system is supported on the support material prior to its introduction into the polymerisation zone. Suitable support materials are, for example, silica, alumina, zirconia, talc, kieselguhr, or magnesia. Impregnation of the support material can be carried out by conventional techniques, for example, by forming a solution or suspension of the catalyst components
- 25 in a suitable diluent or solvent, and slurring the support material therewith. The support material thus impregnated with catalyst can then be separated from the diluent for example, by filtration or evaporation techniques. Once the polymer product is discharged from the reactor, any associated and absorbed hydrocarbons are substantially removed, or degassed, from the polymer by, for example, pressure let-down or gas purging using
- 30 fresh or recycled steam, nitrogen or light hydrocarbons (such as ethylene). Recovered gaseous or liquid hydrocarbons may be recycled to the polymerisation zone.

In the slurry phase polymerisation process the solid particles of catalyst, or

supported catalyst, are fed to a polymerisation zone either as dry powder or as a slurry in the polymerisation diluent. The polymerisation diluent is compatible with the polymer(s) and catalyst(s), and may be an alkane such as hexane, heptane, isobutane, or a mixture of hydrocarbons or paraffins. Preferably the particles are fed to a polymerisation zone as a suspension in the polymerisation diluent. The polymerisation zone can be, for example, an autoclave or similar reaction vessel, or a continuous loop reactor, e.g. of the type well-known in the manufacture of polyethylene by the Phillips Process. When the polymerisation process of the present invention is carried out under slurry conditions the polymerisation is preferably carried out at a temperature above 0°C, most preferably above 15°C. The polymerisation temperature is preferably maintained below the temperature at which the polymer commences to soften or sinter in the presence of the polymerisation diluent. If the temperature is allowed to go above the latter temperature, fouling of the reactor can occur. Adjustment of the polymerisation within these defined temperature ranges can provide a useful means of controlling the average molecular weight of the produced polymer. A further useful means of controlling the molecular weight is to conduct the polymerisation in the presence of hydrogen gas which acts as chain transfer agent. Generally, the higher the concentration of hydrogen employed, the lower the average molecular weight of the produced polymer.

In bulk polymerisation processes, liquid monomer such as propylene is used as the polymerisation medium.

Methods for operating gas phase polymerisation processes are well known in the art. Such methods generally involve agitating (e.g. by stirring, vibrating or fluidising) a bed of catalyst, or a bed of the target polymer (i.e. polymer having the same or similar physical properties to that which it is desired to make in the polymerisation process) containing a catalyst, and feeding thereto a stream of monomer at least partially in the gaseous phase, under conditions such that at least part of the monomer polymerises in contact with the catalyst in the bed. The bed is generally cooled by the addition of cool gas (e.g. recycled gaseous monomer) and/or volatile liquid (e.g. a volatile inert hydrocarbon, or gaseous monomer which has been condensed to form a liquid). The polymer produced in, and isolated from, gas phase processes forms directly a solid in the polymerisation zone and is free from, or substantially free from liquid. As is well known to those skilled in the art, if any liquid is allowed to enter the polymerisation zone of a

gas phase polymerisation process the quantity of liquid in the polymerisation zone is small in relation to the quantity of polymer present. This is in contrast to "solution phase" processes wherein the polymer is formed dissolved in a solvent, and "slurry phase" processes wherein the polymer forms as a suspension in a liquid diluent.

5 The gas phase process can be operated under batch, semi-batch, or so-called "continuous" conditions. It is preferred to operate under conditions such that monomer is continuously recycled to an agitated polymerisation zone containing polymerisation catalyst, make-up monomer being provided to replace polymerised monomer, and continuously or intermittently withdrawing produced polymer from the polymerisation
10 zone at a rate comparable to the rate of formation of the polymer, fresh catalyst being added to the polymerisation zone to replace the catalyst withdrawn from the polymerisation zone with the produced polymer.

For typical production of impact copolymers, homopolymer formed from the first monomer in a first reactor is reacted with the second monomer in a second reactor. For
15 manufacture of propylene/ethylene impact copolymer in a gas-phase process, propylene is polymerised in a first reactor; reactive polymer transferred to a second reactor in which ethylene or other comonomer is added. The result is an intimate mixture of a isotactic polypropylene chains with chains of a random propylene/ethylene copolymer. A random copolymer typically is produced in a single reactor in which a minor amount of a
20 comonomer (typically ethylene) is added to polymerizing chains of propylene.

Methods for operating gas phase fluidised bed processes for making polyethylene, ethylene copolymers and polypropylene are well known in the art. The process can be operated, for example, in a vertical cylindrical reactor equipped with a perforated distribution plate to support the bed and to distribute the incoming fluidising gas stream
25 through the bed. The fluidising gas circulating through the bed serves to remove the heat of polymerisation from the bed and to supply monomer for polymerisation in the bed. Thus the fluidising gas generally comprises the monomer(s) normally together with some inert gas (e.g. nitrogen or inert hydrocarbons such as methane, ethane, propane, butane, pentane or hexane) and optionally with hydrogen as molecular weight modifier. The hot
30 fluidising gas emerging from the top of the bed is led optionally through a velocity reduction zone (this can be a cylindrical portion of the reactor having a wider diameter) and, if desired, a cyclone and or filters to disentrain fine solid particles from the gas

stream. The hot gas is then led to a heat exchanger to remove at least part of the heat of polymerisation. Catalyst is preferably fed continuously or at regular intervals to the bed. At start up of the process, the bed comprises fluidisable polymer which is preferably similar to the target polymer. Polymer is produced continuously within the bed by the polymerisation of the monomer(s). Preferably means are provided to discharge polymer from the bed continuously or at regular intervals to maintain the fluidised bed at the desired height. The process is generally operated at relatively low pressure, for example, at 10 to 50 bars, and at temperatures for example, between 50 and 120 °C. The temperature of the bed is maintained below the sintering temperature of the fluidised polymer to avoid problems of agglomeration.

In the gas phase fluidised bed process for polymerisation of olefins the heat evolved by the exothermic polymerisation reaction is normally removed from the polymerisation zone (i.e. the fluidised bed) by means of the fluidising gas stream as described above. The hot reactor gas emerging from the top of the bed is led through one or more heat exchangers wherein the gas is cooled. The cooled reactor gas, together with any make-up gas, is then recycled to the base of the bed. In the gas phase fluidised bed polymerisation process of the present invention it is desirable to provide additional cooling of the bed (and thereby improve the space time yield of the process) by feeding a volatile liquid to the bed under conditions such that the liquid evaporates in the bed thereby absorbing additional heat of polymerisation from the bed by the "latent heat of evaporation" effect. When the hot recycle gas from the bed enters the heat exchanger, the volatile liquid can condense out. In one embodiment of the present invention the volatile liquid is separated from the recycle gas and reintroduced separately into the bed. Thus, for example, the volatile liquid can be separated and sprayed into the bed. In another embodiment of the present invention the volatile liquid is recycled to the bed with the recycle gas. Thus the volatile liquid can be condensed from the fluidising gas stream emerging from the reactor and can be recycled to the bed with recycle gas, or can be separated from the recycle gas and then returned to the bed.

The method of condensing liquid in the recycle gas stream and returning the mixture of gas and entrained liquid to the bed is described in EP-A-0089691 and EP-A-0241947. It is preferred to reintroduce the condensed liquid into the bed separate from the recycle gas using the process described in our US Patent 5541270, the teaching of

which is hereby incorporated into this specification.

When using the catalysts of the present invention under gas phase polymerisation conditions, the catalyst, or one or more of the components employed to form the catalyst can, for example, be introduced into the polymerisation reaction zone in liquid form, for example, as a solution in an inert liquid diluent. Thus, for example, the transition metal component, or the activator component, or both of these components can be dissolved or slurried in a liquid diluent and fed to the polymerisation zone. Under these circumstances it is preferred the liquid containing the component(s) is sprayed as fine droplets into the polymerisation zone. The droplet diameter is preferably within the range 1 to 1000 microns. EP-A-0593083, the teaching of which is hereby incorporated into this specification, discloses a process for introducing a polymerisation catalyst into a gas phase polymerisation. The methods disclosed in EP-A-0593083 can be suitably employed in the polymerisation process of the present invention if desired.

Although not usually required, upon completion of polymerization or copolymerization, or when it is desired to terminate polymerization or copolymerization or at least temporarily deactivate the catalyst or catalyst component of this invention, the catalyst can be contacted with water, alcohols, acetone, or other suitable catalyst deactivators a manner known to persons of skill in the art.

Homopolymerisation of ethylene with the catalysts of the invention may produce so-called "high density" grades of polyethylene. These polymers have relatively high stiffness and are useful for making articles where inherent rigidity is required. Copolymerisation of ethylene with higher 1-olefins (eg butene, hexene or octene) can provide a wide variety of copolymers differing in density and in other important physical properties. Particularly important copolymers made by copolymerising ethylene with higher 1-olefins with the catalysts of the invention are the copolymers having a density in the range of 0.91 to 0.93. These copolymers which are generally referred to in the art as linear low density polyethylene, are in many respects similar to the so called low density polyethylene produced by the high pressure free radical catalysed polymerisation of ethylene. Such polymers and copolymers are used extensively in the manufacture of flexible blown film.

Propylene polymers produced by the process of the invention include propylene homopolymer and copolymers of propylene with less than 50 mole % ethylene or other

alpha-olefin such as butene-1, pentene-1, 4-methylpentene-1, or hexene-1, or mixtures thereof. Propylene polymers also may include copolymers of propylene with minor amounts of a copolymerizable monomer. Typically, most useful are normally-solid polymers of propylene containing polypropylene crystallinity, random copolymers of
5 propylene with up to about 10 wt.% ethylene, and impact copolymers containing up to about 20 wt.% ethylene or other alpha-olefin. Polypropylene homopolymers may contain a small amount (typically below 2 wt.%) of other monomers to the extent the properties of the homopolymer are not affected significantly.

Propylene polymers may be produced which are normally solid, predominantly
10 isotactic, poly α -olefins. Levels of stereorandom by-products are sufficiently low so that useful products can be obtained without separation thereof. Typically, useful propylene homopolymers show polypropylene crystallinity and have isotactic indices above 90 and many times above 95. Copolymers typically will have lower isotactic indices, typically above 80-85.

15 Depending upon polymerization conditions known in the art, propylene polymers with melt flow rates from below 1 to above 1000 may be produced in a reactor. For many applications, polypropylenes with a MFR from 2 to 100 are typical. Some uses such as for spunbonding may use a polymer with an MFR of 500 to 2000.

Peroxide compounds may be added to ethylene or propylene polymers. For
20 ethylene based polymers, peroxides can be used to give cross-linking in the polymer. For the preparation of high MFR propylene polymers, peroxide compounds may be added during extrusion for controlled rheology to increase the melt flow rate of polymer. Peroxide acts to break long polymer chains and has the effect of both increasing MFR and narrowing the molecular weight distribution (M_w/M_n) or polydispersity. A typical
25 reactor polypropylene powder with an MFR of 2g/10 min. by controlled rheology treatment with peroxide in an extruder may form a polymer with an MFR of 20-40. By varying the type, amount of, and process conditions using, peroxide, the final polymer MFR may be controlled as known in the art.

Depending upon the use of the polymer product, minor amounts of additives are
30 typically incorporated into the polymer formulation such as acid scavengers, antioxidants, stabilizers, and the like. Generally, these additives are incorporated at levels of about 25 to 2000 ppm, typically from about 50 to about 1000 ppm, and more

typically 400 to 1000 ppm, based on the polymer.

In use, polymers or copolymers made according to the invention in the form of a powder are conventionally compounded into pellets. Examples of uses for polymer compositions made according to the invention include use to form fibres, extruded films, tapes, spunbonded webs, moulded or thermoformed products, and the like. The polymers may be blown into films, or may be used for making a variety of moulded or extruded articles such as pipes, and containers such as bottles or drums. Specific additive packages for each application may be selected as known in the art. Examples of supplemental additives include slip agents, anti-blocks, anti-stats, mould release agents, primary and secondary anti-oxidants, clarifiers, nucleants, uv stabilizers, and the like. Classes of additives are well known in the art and include phosphite antioxidants, hydroxylamine (such as N,N-dialkyl hydroxylamine) and amine oxide (such as dialkyl methyl amine oxide) antioxidants, hindered amine light (uv) stabilizers, phenolic stabilizers, benzofuranone stabilizers, and the like. Various olefin polymer additives are described in U.S. patents 4,318,845, 4,325,863, 4,590,231, 4,668,721, 4,876,300, 5,175,312, 5,276,076, 5,326,802, 5,344,860, 5,596,033, and 5,625,090.

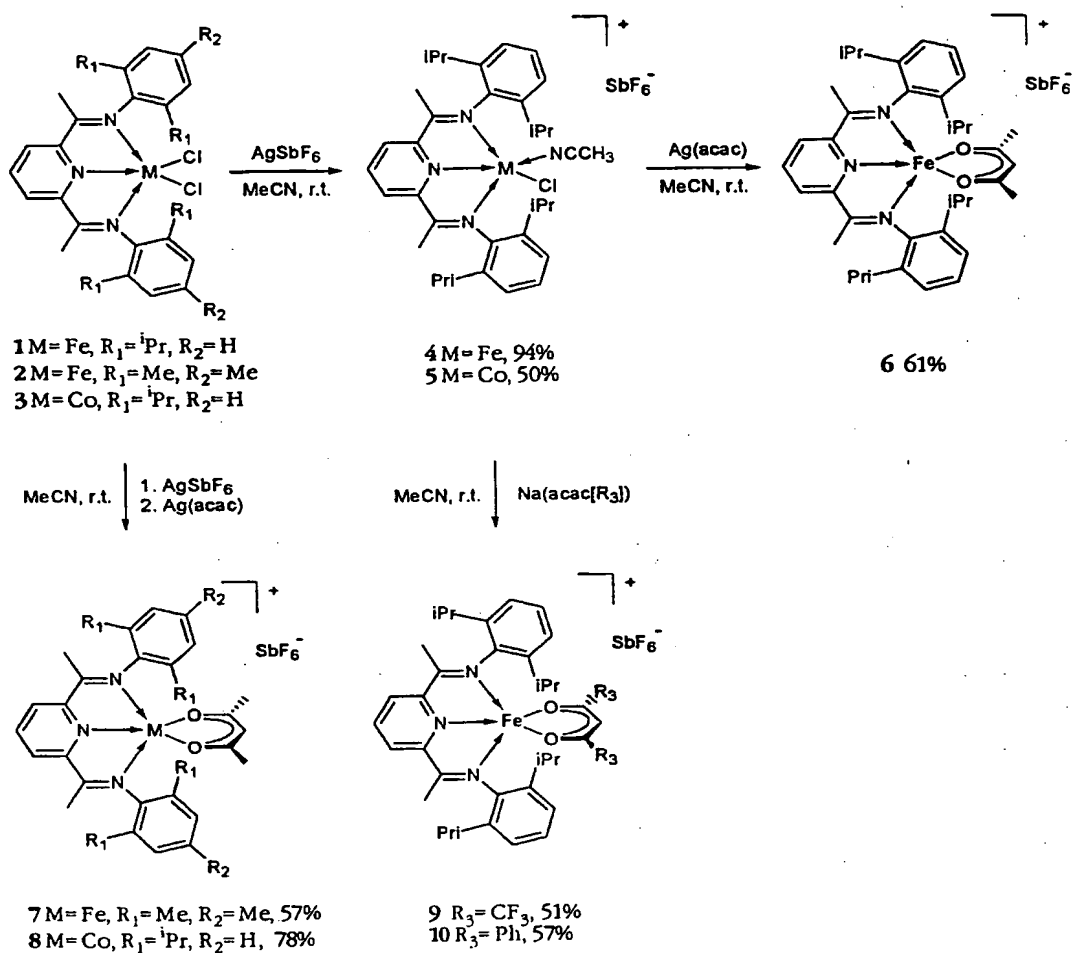
Fillers such as silica, glass fibers, talc, and the like, nucleating agents, and colourants also may be added to the polymer compositions as known by the art.

The present invention is illustrated in the following Examples and the accompanying drawings.

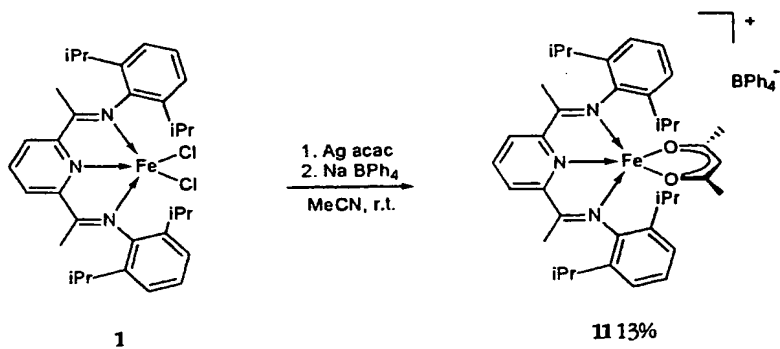
EXAMPLES

The parent tridentate 2,6 bis(imino)pyridine dichloro complexes **1 - 3** were prepared according to the literature. AgSbF₆ and Ag acac were purchased from Aldrich. Acetonitrile (MeCN), pentane and dichloromethane (DCM) were distilled over CaH₂; diethylether (Et₂O) was distilled over sodium prior to use. The cationic Fe and Co complexes **4 - 11** were prepared as shown in schemes 1 and 2.

Scheme 1: Synthesis of **4 - 10**



Scheme 2: Synthesis of 11



EXAMPLE 1 - Synthesis of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl] pyridine iron(II) chloride hexa-fluoroantimonate acetonitrile adduct (4)

Silver hexafluoroantimonate (1.22 g, 2.0 mmol) and 1 (687 mg, 2.00 mmol) were dissolved in 50 ml MeCN. A white precipitate in a dark red solution was formed immediately. After stirring at room temperature overnight the solution was filtered off and the solvent was removed *in vacuo*. The residue was washed with Et₂O (2×30 ml). After drying *in vacuo* a red powder was obtained.

Yield: 1.59 g (94%). ¹H-NMR (250 MHz, CD₂Cl₂, r.t., all peaks appear as broad singlets): δ -14.17 (1H, Py-H_p), -13.29 (2H, Ph-H_p), -8.87 (6H, N=C-Me), -2.29 (24H, iPr-Me), 12.46 (4H, iPr-CH or Ph-H_m), 14.78 (4H, Ph-H_m or iPr-CH), 101.45 (2H, Py-H_m). IR (neat compound): 3064 (w, ν(C-H)_{Ar}), 2964 (s, ν(CH₃)_{as}), 2929 (m, ν(CH₃)), 2872 (m, ν(CH₃)_s), 1617 (m, ν(C=N)), 1581 (s, ν(C-C)_{Py}), 1460 (m, ν(C-C)_{Ph} or δ(CH₃)_{as}), 1443 (m, ν(C-C)_{Ph} or δ(CH₃)_{as}), 1368 (m, δ(CH₃)_s), 1262 (s), 802 (s, δ(C-H)_{Ar}), 781 (s, δ(C-H)_{Ar}), 737 (s, δ(C-H)_{Ar}), 670 (s, ν(Sb-F)) cm⁻¹. FAB-MS (m/e): 572 (100%), 556 (10%).

EXAMPLE 2 - Synthesis of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl] pyridine cobalt(II) chloride hexafluoroantimonate acetonitrile adduct (5)

Silver hexafluoroantimonate (157 mg, 0.46 mmol) and 3 (280 mg, 0.46 mmol) were dissolved in 30 ml MeCN. A white precipitate in a green solution was formed immediately. After stirring at room temperature overnight, the solvent was removed *in vacuo*. The residue was extracted with DCM. The solvent was pumped off and the product was washed with Et₂O (1×20 ml). After drying *in vacuo* a green powder was obtained. Crystals suitable for X-ray analysis were grown *via* crystallisation from a concentrated DCM solution of the crude reaction product in the preparation of 8 layered with pentane.

Yield: 220 mg (50%). ¹H-NMR (250 MHz, CD₂Cl₂, r.t., all peaks appear as broad singlets): δ -69.90 (4H, iPr-CH or Ph-H_m), -27.59 (4H, Ph-H_m or iPr-CH), -23.58 (12H, iPr-Me), -19.48 (12H, iPr-Me), -4.64 (2H, Ph-H_p), 15.24 (6H, N=C-Me), 49.42 (1H, Py-H_p), 125.98 (2H, Py-H_m). IR (neat compound): 3063 (w, ν(C-H)_{Ar}), 2966 (s, ν(CH₃)_{as}), 2931 (m, ν(CH₃)), 2871 (w, ν(CH₃)_s), 1618 (w, ν(C=N)), 1587 (s, ν(C-C)_{Py}), 1467 (s, ν(C-C)_{Ph} or δ(CH₃)_{as}), 1441 (s, ν(C-C)_{Ph} or δ(CH₃)_{as}), 1374 (s, δ(CH₃)_s), 1264

(s), 838 (w, $\delta(\text{C-H})_{\text{Ar}}$), 798 (s, $\delta(\text{C-H})_{\text{Ar}}$), 777 (s, $\delta(\text{C-H})_{\text{Ar}}$), 761(w, $\delta(\text{C-H})_{\text{Ar}}$), 744 (w, $\delta(\text{C-H})_{\text{Ar}}$), 662 (s, $\nu(\text{Sb-F})$) cm^{-1} . FAB-MS (m/e): 575 (100%), 540 (45%). $\mu_{\text{eff}} = 4.6 \text{ BM}$ (Evans' method).

Crystal data for 5: $\text{C}_{35}\text{H}_{46}\text{N}_4\text{CoSbF}_6 \times 1.5 \text{ CH}_2\text{Cl}_2$, $M = 980.82$, monoclinic, C2/c ,
 5 $a = 25.879(5) \text{ \AA}$, $b = 10.073(2) \text{ \AA}$, $c = 36.573(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 93.011(12)^\circ$, $\gamma = 90^\circ$,
 $V = 9521(3) \text{ \AA}^3$, $Z = 8$, $D_c = 1.368 \text{ g/cm}^3$, $\mu(\text{Cu-K}\alpha) = 53.6 \text{ cm}^{-1}$, $F(000) = 3968$, crystal
 morphology = orange/red prism, crystal size = $0.37 \times 0.33 \times 0.17 \text{ mm}$, independent
 reflexes = 6327, $R_1 = 0.076$.

EXAMPLE 3 - Synthesis of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]
 10 pyridine iron(II) acetylacetonate hexafluoroantimonate (6)

Silver acetylacetonate (150 mg, 0.72 mmol) and 4 (540 mg, 0.64 mmol) were
 dissolved in 20 ml MeCN. A white precipitate in a dark red solution was formed
 immediately. After stirring at room temperature overnight, the solution was filtered off
 and the solvent was removed *in vacuo*. The red residue was redissolved in 20 ml DCM
 15 and precipitated with 60 ml pet. ether. The supernatant solution was filtered off and the
 residue was washed with pet. ether (2x20 ml) and dried *in vacuo* and isolated as a red
 powder. Crystals suitable for X-ray analysis were grown *via* crystallisation from a
 concentrated DCM solution layered with pentane.

Yield: 340 mg (61 %). $^1\text{H-NMR}$ (250 MHz, CD_2Cl_2 , r.t., all peaks appear as broad
 20 singlets): δ -60.71 (6H, $\text{N}=\text{C-Me}$), -33.12 (1H, $\text{O}=\text{C-CH}$ or Py-H_p), -22.33 (4H, Ph-H_m
 or iPr-CH), -12.70 (2H, Ph-H_p), -6.02 (12H, iPr-Me), -2.85 (12H, iPr-Me), 2.34 (6H,
 $\text{O}=\text{C-Me}$), 13.05 (4H, iPr-CH or Ph-H_m), 30.50 (1H, Py-H_p or $\text{O}=\text{C-CH}$), 117.54 (2H,
 Py-H_m). IR (neat compound): 3064 (w, $\nu(\text{C-H})_{\text{Ar}}$), 2967 (m, $\nu(\text{CH}_3)_{\text{as}}$), 2930 (w, ν
 (CH₃)), 2872 (w, $\nu(\text{CH}_3)_s$), 1625 (w, $\nu(\text{C}=\text{N})$), 1588 (m, $\nu(\text{C-C})_{\text{Py}}$), 1567 (s, $\nu(\text{C}\approx\text{C}) + \nu$
 25 ($\text{C}\approx\text{O}$)), 1522 (s, $\nu(\text{C}\approx\text{C}) + \nu(\text{C}\approx\text{O})$), 1467 (m, $\nu(\text{C-C})_{\text{Ph}}$ or $\delta(\text{CH}_3)_{\text{as}}$), 1440 (m, ν
 ($\text{C-C})_{\text{Ph}}$ or $\delta(\text{CH}_3)_{\text{as}}$), 1369 (s, $\delta(\text{CH}_3)_s$), 1261 (m), 816 (w, $\delta(\text{C-H})_{\text{Ar}}$), 795 (w, $\delta(\text{C-H})_{\text{Ar}}$),
 776 (m, $\delta(\text{C-H})_{\text{Ar}}$), 758 (w, $\delta(\text{C-H})_{\text{Ar}}$), 742 (w, $\delta(\text{C-H})_{\text{Ar}}$), 659 (s, $\nu(\text{Sb-F})$) cm^{-1} .
 FAB-MS (m/e): 636 (100%), 620 (10%). Anal. Calcd. for $\text{C}_{38}\text{H}_{50}\text{N}_3\text{O}_2\text{FeSbF}_6 \times 1$
 CH_2Cl_2 : C, 48.93; H, 5.47; N, 4.39. Found: C, 49.11; H, 5.33; N, 4.33. $\mu_{\text{eff}} = 5.0 \text{ BM}$
 30 (Evans' method) and 4.8 BM (Evan's balance).

Crystal data for 6: $C_{38}H_{50}N_3O_2FeSbF_6 \times 2 CH_2Cl_2$, $M = 1024.26$, monoclinic, $P2_1/c$, $a = 15.005(2) \text{ \AA}$, $b = 16.903(2) \text{ \AA}$, $c = 18.815(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 94.950(9)^\circ$, $\gamma = 90^\circ$, $V = 4754.3(4) \text{ \AA}^3$, $Z = 4$, $D_c = 1.456 \text{ g/cm}^3$, $\mu(\text{Cu-K}\alpha) = 53.6 \text{ cm}^{-1}$, $F(000) = 2120$, crystal morphology = orange/red prism, crystal size = $0.77 \times 0.73 \times 0.33 \text{ mm}$,

5 independent reflexes = 8301, $R_1 = 0.0656$.

EXAMPLE 4 - Synthesis of 2,6-bis-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine iron(II) acetylacetonate hexafluoroantimonate (7)

Silver hexafluoroantimonate (686 mg, 2.0 mmol) and 2 (1.04 mg, 2.0 mmol) were dissolved in 80 ml MeCN. A beige precipitate in a red solution was formed immediately. After stirring at room temperature for 1.5 hours, a suspension of silver acetylacetonate (454 mg, 2.2 mmol) in 10 ml MeCN was added. The reaction mixture was stirred at r.t. overnight. The solution was then filtered off and the solvent was removed *in vacuo*. The product was redissolved in 20 ml DCM and precipitated by adding pentane. The solution was filtered off and the residue was washed with a mixture of 15% DCM/Et₂O (2x30ml) to remove all excess silver acetylacetonate. After drying *in vacuo* a red powder was obtained.

Yield: 900 mg (57 %). ¹H-NMR (250 MHz, CD₂Cl₂, r.t., all peaks appear as broad singlets): δ -64.22 (6H, N=C-Me), -34.10 (1H, O=C-CH or Py-H_p), -7.88 (6H, O=C-Me), 1.90 (12H, Ph-Me_m), 14.43 (4H, Ph-H), 24.00 (6H, Ph-Me_p), 60.50 (1H, Py-H_p or O=C-CH), 131.97 (2H, Py-H_m). IR (neat compound): 3104 (w, $\nu(\text{C-H})_{Ar}$), 3002 (w, $\nu(\text{C-H})_{Ar}$), 2957 (w, $\nu(\text{CH}_3)$), 2957 (w, $\nu(\text{CH}_3)_{as}$), 2920 (w, $\nu(\text{CH}_3)$), 2858 (w, $\nu(\text{CH}_3)_s$), 2741 (w), 1624 (w, $\nu(\text{C=N})$), 1591 (m, $\nu(\text{C-C})_{Py}$), 1555 (s, $\nu(\text{C}\approx\text{C}) + \nu(\text{C}\approx\text{O})$), 1521 (s, $\nu(\text{C}\approx\text{C}) + \nu(\text{C}\approx\text{O})$), 1479 (m, $\nu(\text{C-C})_{Ph}$ or $\delta(\text{CH}_3)_{as}$), 1434 (w, $\nu(\text{C-C})_{Ph}$ or $\delta(\text{CH}_3)_{as}$), 1362 (s, $\delta(\text{CH}_3)_s$), 1260 (s), 1226 (s), 857 (w, $\delta(\text{C-H})_{Ar}$), 816 (w, $\delta(\text{C-H})_{Ar}$), 790 (w, $\delta(\text{C-H})_{Ar}$), 743 (w, $\delta(\text{C-H})_{Ar}$), 657 (s, $\nu(\text{Sb-F})$) cm⁻¹. FAB-MS (m/e): 552 (100%). Anal. Calcd. for $C_{32}H_{38}N_3O_2FeSbF_6 \times 0.5 CH_2Cl_2$: C, 46.82; H, 4.71; N, 5.04. Found: C, 47.02; H, 4.38; N, 4.99. $\mu_{eff} = 5.2 \text{ BM}$ (Evans' method).

EXAMPLE 5 - Synthesis of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridine cobalt(II) acetylacetonate hexafluoroantimonate (8)

30 Silver hexafluoroantimonate (640 mg, 1.9 mmol) and 3 (1.14 g mg, 1.9 mmol) were dissolved in 50 ml MeCN. A grey precipitate in a green solution was formed

immediately. After stirring at room temperature for one hour, a suspension of silver acetylacetonate (384 mg, 1.9 mmol) in 10 ml MeCN was added. The colour of the solution changed immediately to red. The reaction mixture was stirred at r.t. overnight. The solution was filtered off and the residue was washed with Et₂O (2×30 ml) and dried *in vacuo* to obtain a beige powder.

Yield: 1.30g (78 %). ¹H-NMR analysis of the product showed the presence of the intermediate compound 5 as an impurity. The crude product (1.11g, ≈1.3 mmol) was therefore treated with silver acetylacetonate (40 mg, 0.2 mmol) in 30 ml DCM at r.t. for 16 h. The solution was concentrated and the product precipitated by addition of pentane. The solution was filtered off and the residue was washed with Et₂O (2×20 ml) to obtain a beige powder.

Yield: 890 mg (53%). ¹H-NMR (250 MHz, CD₂Cl₂, r.t., all peaks appear as broad singlets): δ -73.36 (4H, iPr-CH or Ph-H_m), -34.90 (1H, O=C-CH or Py-H_p), -12.25 (12H, iPr-Me), -11.56 (12H, iPr-Me), -9.82 (2H, Ph-H_p), -8.83 (6H, O=C-Me), 10.33 (6H, N=C-Me), 15.41 (4H, Ph-H_m or iPr-CH), 34.96 (1H, Py-H_p or O=C-CH), 115.72 (2H, Py-H_m). IR (neat compound): 3064 (w, ν(C-H)_{Ar}), 2967 (s, ν(CH₃)_{as}), 2931 (m, ν(CH₃)), 2873 (w, ν(CH₃)_s), 1624 (w, ν(C=N)), 1578 (s, ν(C≈C) + ν(C≈O)), 1522 (s, ν(C≈C) + ν(C≈O)), 1468 (m, ν(C-C)_{Ph} or δ(CH₃)_{as}), 1441 (m, ν(C-C)_{Ph} or δ(CH₃)_{as}), 1372(s, δ(CH₃)_s), 1265 (s), 816 (w, δ(C-H)_{Ar}), 797 (m, δ(C-H)_{Ar}), 777 (m, δ(C-H)_{Ar}), 758 (w, δ(C-H)_{Ar}), 742 (w, δ(C-H)_{Ar}), 659 (s, ν(Sb-F)) cm⁻¹. FAB-MS (m/e): 639 (100%), 623 (5%) 540 (8%). Anal. Calcd. for C₃₈H₅₀N₃O₂CoSbF₆ × 2 CH₂Cl₂: C, 45.96; H, 5.21; N, 4.02. Found: C, 45.41; H, 4.93; N, 4.21. μ_{eff} = 4.6 BM (Evans' method).

EXAMPLE 6 - Synthesis of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridine iron(II) 1,3-trifluoro-methyl-1,3-propanedionate hexafluoroantimonate (9)

Sodium 1,3-trifluoromethyl-1,3-propanedionate (46 mg, 0.20 mmol) and 4 (170 mg, 0.20 mmol) were dissolved in a mixture of 30 ml Et₂O and 10 ml DCM to dissolve both starting materials. After stirring at r.t. overnight the solvent was pumped off and the residue was extracted with DCM. After removal of the solvent *in vacuo* a purple powder was obtained.

Yield: 100 mg (51 %). IR (neat compound): 3066 (w, ν(C-H)_{Ar}), 2967 (m, ν(CH₃)_{as}), 2932 (w, ν(CH₃)), 2872 (w, ν(CH₃)_s), 1625 (w, ν(C=N)), 1590 (m, ν(C-C)_{Py}),

1552 (w, $\nu(\text{C}\equiv\text{C}) + \nu(\text{C}\approx\text{O})$), 1522 (w, $\nu(\text{C}\equiv\text{C}) + \nu(\text{C}\approx\text{O})$), 1469 (m, $\nu(\text{C}-\text{C})_{\text{Ph}}$ or $\delta(\text{CH}_3)_{\text{as}}$), 1436 (m, $\nu(\text{C}-\text{C})_{\text{Ph}}$ or $\delta(\text{CH}_3)_{\text{as}}$), 1373 (s, $\delta(\text{CH}_3)_{\text{s}}$), 1256 (s), 1206 (s, $\nu(\text{CF}_3)$), 1147 (s, $\nu(\text{CF}_3)$), 815 (w, $\delta(\text{C}-\text{H})_{\text{Ar}}$), 795 (m, $\delta(\text{C}-\text{H})_{\text{Ar}}$), 776 (w, $\delta(\text{C}-\text{H})_{\text{Ar}}$), 759 (w, $\delta(\text{C}-\text{H})_{\text{Ar}}$), 741 (w, $\delta(\text{C}-\text{H})_{\text{Ar}}$), 660 (s, $\nu(\text{Sb}-\text{F})$) cm^{-1} . FAB-MS (m/e): 744 (100%), 728

5 (8%). $\mu_{\text{eff}} = 5.3$ BM (Evans' method).

EXAMPLE 7 - Synthesis of sodium 1,3-diphenyl-1,3-propanedionate

Dibenzoylmethane (8.10g, 36.1mmol) was dissolved in 50ml THF and added dropwise *via* a cannula to a suspension of sodiumhydride (2.33 g, 97 mmol) in 50 ml THF. After the addition was complete the reaction mixture was stirred at r.t. overnight.

10 The solution was filtered off and concentrated *in vacuo*. The product was precipitated by addition of pentane and washed with pentane (2x50 ml). After drying *in vacuo* a yellow powder was obtained which is insoluble in DCM, Et₂O and only poorly soluble in toluene but soluble in MeCN. Yield: 7.82 g (88%). ¹H-NMR (250 MHz, d₈-THF, r.t.): δ 6.50 (s, 1H, O=CC-H), 7.28 (m, 6H, Ph-H), 7.95 (m, 4H, Ph-H).

15 EXAMPLE 8 - Synthesis of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl] pyridine iron(II) 1,3-diphenyl-1,3-propanedionate hexafluoroantimonate (10)

Sodium 1,3-diphenyl-1,3-propanedionate (74 mg, 0.30 mmol) and 4 (250 mg, 0.30 mmol) were dissolved in 40 ml MeCN. After stirring at r.t. overnight the solvent was pumped off and the red residue was extracted with DCM. After removal of the solvent

20 *in vacuo* a purple powder was obtained.

Yield: 170 mg (57 %). IR (neat compound): 3062 (w, $\nu(\text{C}-\text{H})_{\text{Ar}}$), 2965 (m, $\nu(\text{CH}_3)_{\text{as}}$), 2928 (w, $\nu(\text{CH}_3)$), 2870 (w, $\nu(\text{CH}_3)_{\text{s}}$), 1624 (w, $\nu(\text{C}=\text{N})$), 1589 (m, $\nu(\text{C}-\text{C})_{\text{Py}}$), 1522 (s, $\nu(\text{C}\equiv\text{C}) + \nu(\text{C}\approx\text{O})$), 1479 (s, $\nu(\text{C}-\text{C})_{\text{Ph}}$ or $\delta(\text{CH}_3)_{\text{as}}$), 1440 (m, $\nu(\text{C}-\text{C})_{\text{Ph}}$ or $\delta(\text{CH}_3)_{\text{as}}$), 1353 (s, $\delta(\text{CH}_3)_{\text{s}}$), 1261 (m), 816 (w, $\delta(\text{C}-\text{H})_{\text{Ar}}$), 794 (w, $\delta(\text{C}-\text{H})_{\text{Ar}}$), 773 (w, $\delta(\text{C}-\text{H})_{\text{Ar}}$), 758 (w, $\delta(\text{C}-\text{H})_{\text{Ar}}$), 722 (w, $\delta(\text{C}-\text{H})_{\text{Ar}}$), 658 (s, $\nu(\text{Sb}-\text{F})$) cm^{-1} . FAB-MS (m/e): 760 (100%), 744 (10%). $\mu_{\text{eff}} = 5.4$ BM (Evans' method).

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EXAMPLE 9 - Synthesis of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl] pyridine iron(II) acetylacetonate tetraphenylborate (11)

Silver acetylacetonate (225 mg, 1.09 mmol) and 1 (639 mg, 1.05 mmol) were dissolved in 30 ml MeCN. A dark precipitate in a green solution was formed

30 immediately. After stirring at r.t. for one hour, the solution was filtered into a solution of

sodium tetraphenylborate in 20 ml MeCN. The colour of the solution immediately changed to red. Further extractions of the dark residue with MeCN were also added. After stirring at r.t. overnight, the solvent was removed *in vacuo* and the product was dissolved in DCM to obtain a red solution with a white precipitate. The solution was
 5 filtered off and concentrated to 5 ml. The product was precipitated by addition of pentane. After filtration and drying *in vacuo* a red-brown powder was obtained.

Yield: 130 mg (13%). ¹H-NMR (250 MHz, CD₂Cl₂, r.t., all peaks appear as broad singlets): δ -61.46 (6H, N=C-Me), -34.47 (1H, O=C-CH or Py-H_p), -22.73 (4H, Ph-H_m or iPr-CH), -12.84 (2H, Ph-H_p), -5.99 (12H, iPr-Me), -2.86 (12H, iPr-Me), 2.25 (6H, O=C-Me), 6.98 (4H, BPh-H), 7.40 (8H, BPh-H), 8.52 (8H, BPh-H), 13.10 (4H, iPr-CH or Ph-H_m), 30.40 (1H, Py-H_p or O=C-CH), 117.77 (2H, Py-H_m). IR (neat compound):
 10 3055 (m, ν(C-H)_{Ar}), 3033 (w, ν(C-H)_{Ar}), 2999 (w, ν(C-H)_{Ar}), 2964 (m, ν(CH₃)_{as}), 2927 (w, ν(CH₃)), 2870 (w, ν(CH₃)_s), 1621 (w, ν(C=N)), 1581 (m, ν(C-C)_{Py}), 1557 (s, ν(C≈C) + ν(C≈O)), 1522 (s, ν(C≈C) + ν(C≈O)), 1479 (m, ν(C-C)_{Ph} or δ(CH₃)_{as}), 1426 (m, ν
 15 (C-C)_{Ph} or δ(CH₃)_{as}), 1367 (s, δ(CH₃)_s), 1259 (m), 845 (w, δ(C-H)_{Ar}), 794 (w, δ(C-H)_{Ar}), 775 (m, δ(C-H)_{Ar}), 743 (s, δ(C-H)_{Ar}), 733 (s, δ(C-H)_{Ar}), 706 (s, δ(C-H)_{Ar}) cm⁻¹.
 FAB-MS (m/e): 636 (100%), 620 (8%). μ_{eff} = 5.1 BM (Evans' method).

Ethylene Polymerisation reactions

EXAMPLE 10 - Schlenk test at 1 bar ethylene pressure

20 In a typical experiment, 0.01 mmol of the precatalyst were placed in a Schlenk flask and dissolved in 120 ml toluene. A toluene solution of B(C₆F₅)₃ was added via a syringe followed by a solution of trimethylaluminium in toluene. If the polymerisation was carried out in the presence of a polar olefin, it was added at this stage via a syringe. Then the solution was purged with a steady flow of ethylene at a pressure of 1 bar. After
 25 15 minutes the ethylene flow was stopped and the polymerisation was terminated by adding a small amount of dilute aqueous HCl. The polyethylene was precipitated by the addition of methanol. The solid polyethylene was filtered off and dried *in vacuo* at 40°C overnight. The results are shown in Tables 1 and 2 below.

TABLE 1 (tests in Schlenk tubes)

Catalyst	Activity g/mmol bar.h	M _n	M _w	M _{pk}	PDI	Sat ends /1000 C	Vinyl ends /1000 C	Ratio Sat /Vinyl
4	510	155000	477000	511000	3.1	0.5	0	—
6	1100	40000	117000	88000	2.9	0.54	0.37	1.46
8	410	12000	28000	21000	2.3	1.52	1.24	1.23

Conditions: 120ml toluene, 1 bar, 0.010 mmol catalyst, 1 eq B(C₆F₅)₃, 10 eq TMA, 15 mins

5 TABLE 2 (tests in Schlenk tubes)

Catalyst	Activity g/mmol bar.h	M _n	M _w	M _{pk}	PDI	Sat ends /1000 C	Vinyl ends /1000 C	Ratio Sat /Vinyl
6	970	83000	205000	157000	2.5	0.50	0.18	2.78
8	430	13000	29000	23000	2.3	1.67	1.29	1.29

Conditions: 120ml toluene, 1 bar, 0.010 mmol catalyst, 1 eq B(C₆F₅)₃, 10 eq TMA, 1000 eq MMA, 15 mins

EXAMPLE 11 - Test in Fisher-Porter bottles at 5 bar ethylene pressure

- 10 In a typical experiment, 0.002 or 0.01 mmol of the precatalyst were placed in a Schlenk flask and dissolved in a measured amount of toluene. 100 equiv MAO were added to yield a 0.5 mM solution in total. 4 ml of this solution were transferred via syringe into a Fisher-Porter bottle, filled with 250 ml of toluene. Then the solution was purged with a steady flow of ethylene at a pressure of 5 bar. After 15 minutes the
- 15 ethylene flow was stopped and the polymerisation was terminated by adding a small amount of dilute aqueous HCl. The polyethylene was precipitated by the addition of methanol. The solid polyethylene was filtered off and dried *in vacuo* at 40°C overnight. The results are shown in Tables 3 and 4 below.

TABLE 3 (tests in Fisher-Porter bottles)

Catalyst	Activity g/mmol bar.h	M _n	M _w	M _{pk}	PDI	Sat ends /1000 C	Vinyl ends /1000 C	Ratio Sat /Vinyl
1	11400	46000	169000	87000	3.7	0.33	0.30	1.10
2	17800	14000	96000	23000	6.7	1.35	1.07	1.26
4	4800	33000	112000	82000	3.4	0.47	0.35	1.34
6	5400	52000	136000	10200 0	2.6	0.49	0.43	1.14
7	5600	17000	64000	33000	3.8	1.03	0.86	1.20
9	8100	40000	146000	84000	3.6	0.47	0.39	1.21
10	7400	40000	121000	79000	3.0	0.52	0.38	1.37
11	5700	49000	198000	11100 0	4.1	0.49	0.35	1.40

Conditions: 250 ml toluene, 5 bar, 0.002 mmol catalyst, 100 eq MAO, 15 mins

TABLE 4 (tests in Fisher-Porter bottles)

Catalyst	Activity g/mmol bar.h	M _n	M _w	M _{pk}	PDI	Sat ends /1000 C	Vinyl ends /1000 C	Ratio Sat /Vinyl
3	1400	6300	15000	13000	2.3	2.82	2.19	1.29
5	800	7200	19000	13000	2.6	2.06	2.05	1.00
8	1700	5900	16000	13000	2.7	2.23	2.15	1.04

5 Conditions: 250 ml toluene, 5 bar, 0.010 mmol catalyst, 100 eq MAO, 15 mins

EXAMPLE 12 - Test in 1 litre autoclave at 4 bar (for iron catalysts) and 10 bar (for cobalt catalysts) ethylene pressure

In a typical experiment, 0.005 or 0.006 mmol of the precatalyst were placed in a Schlenk flask and dissolved in a measured amount of toluene. 100 equiv MAO were added to yield a 0.25 mM solution in total. 2 ml of this solution were transferred via

10

- syringe into the autoclave bottle, filled with isobutane solvent. 30 mins prior to the addition of the catalyst solution, 4000 equivalents of triisobutylaluminium were syringed into the autoclave. After addition of the catalyst the autoclave was purged with a steady flow of ethylene at a pressure of 4 bar at a temperature of 50°C. After 60 minutes the ethylene flow was stopped. Upon pressure release the isobutane evaporated and the solid polyethylene could be recovered. The polyethylene was then washed with dilute aqueous HCl and methanol. The solid polyethylene was filtered off and dried *in vacuo* at 40°C overnight. The results are shown in Tables 5 and 6 below.

TABLE 5 (tests in autoclave)

Catalyst	Activity g/mmol bar.h	M _n	M _w	M _{pk}	PDI	Sat ends /1000 C	Vinyl ends /1000 C	Ratio Sat /Vinyl
4	6100	64000	278000	254000	4.3	0.38	0.14	2.71
6	7500	78000	317000	179000	4.1	0.32	0.14	2.28

- Conditions: 500 ml isobutane, 4 bar, 0.0005 mmol catalyst, 4000 eq TiBAI, 100 eq MAO, 1 hour

TABLE 6 (tests in autoclave)

Catalyst	Activity g/mmol bar.h	M _n	M _w	M _{pk}	PDI	Sat ends /1000 C	Vinyl ends /1000 C	Ratio Sat /Vinyl
5	220	4500	12000	8900	2.6	3.76	2.80	1.34
8	320	4600	12000	9100	2.7	2.80	2.60	1.08

Conditions: 500 ml isobutane, 10 bar, 0.0006 mmol catalyst, 4000 eq TiBAI, 1000 eq MAO, 1 hour

EXAMPLE 13 - Further tests in schlenk tubes at 1 bar ethylene pressure

- 0.01 mmol precatalyst 6 was dissolved in 100 ml solvent. The cocatalyst was added and the flask attached to the ethylene line. The polymerisation was quenched after 30 min using acidified methanol. Adding 150 ml of methanol precipitated the polymer produced. The polymer was then filtered off, washed with methanol and dried at 50°C in a vacuum oven. The results are shown in Table 7 below.

TABLE 7

Run	Cocatalyst	Solvent	Activity [g/(mmol bar h)]
1	100 eq MAO	Toluene	800
2	10 eq TMA	Toluene	500
3	1 eq BarF / 20 eq TMA	Toluene	1400
4	1 eq BarF / 10 eq TiBAI	Toluene	100
5	100 eq MAO	Petether / Toluene 90 / 10	610
6	100 eq MAO / 3 eq MAD	Petether / Toluene 90 / 10	1100

BarF=Tris(pentafluorophenyl)

5

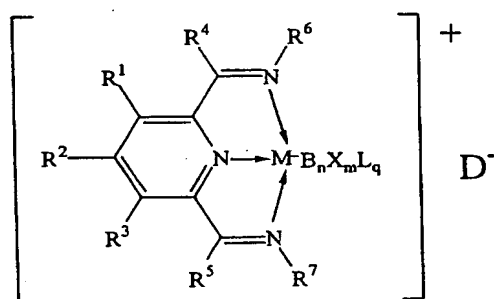
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CLAIMS

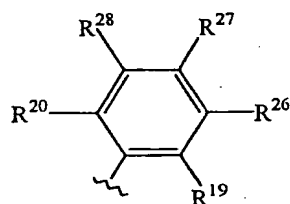
1. Complex having the Formula (I)



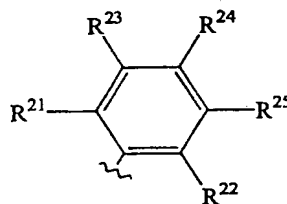
Formula (I)

- wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III], Ru[IV], V[II], V[III], V[IV], V[V], Ti[II], Ti[III] or Ti[IV];
- and R¹ to R⁷ are each independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl or SiR'₃ where each R' is independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, substituted heterohydrocarbyl;
- B is a chelating ligand comprising at least one atom from O, S, N and P bound directly to M; X is a monodentate monoanionic ligand; L is a ligand datively bonded to M; n is greater or equal to 1, m is greater or equal to 0 and q is greater or equal to 0, provided that n and m are integers or zero which satisfy the valency of the metal; and D is a compatible non-coordinating anion.
2. Complex according to claim 1 wherein n = 1, m = 0 and q = 0 or 1.

3. Complex according to claim 1 or 2 wherein R^6 and R^7 are independently selected from phenyl, 1-naphthyl, 2-naphthyl, 2-methylphenyl, 2-ethylphenyl, 2,6-diisopropylphenyl, 2,3-diisopropylphenyl, 2,4-diisopropylphenyl, 2,6-di-n-butylphenyl, 2,6-dimethylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2-t-butylphenyl, 2,6-diphenylphenyl, 2,4,6-trimethylphenyl, 2,6-trifluoromethylphenyl, 4-bromo-2,6-dimethylphenyl, 3,5-dichloro-2,6-diethylphenyl, 2,6-bis(2,6-dimethylphenyl)phenyl, cyclohexyl or pyridinyl.
4. Complex according to any preceding claim wherein R^6 is represented by the group "P" and R^7 is represented by the group "Q" as follows:



Group P



Group Q

- wherein R^{19} to R^{28} are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more of R^1 to R^5 and R^{19} to R^{28} are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents.
5. Complex according to claim 4 wherein at least one of and preferably all of R^{19} , R^{20} , R^{21} and R^{22} are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl.
6. Complex according to any preceding claim wherein R^1 , R^2 , R^3 , R^4 , R^6 and R^{19} to R^{28} are each independently selected from hydrogen and C_1 to C_8 hydrocarbyl.
7. Complex according to claim 5 or 6 wherein R^{19} , R^{20} , R^{21} and R^{22} are independently selected from methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, tert.-butyl, n-pentyl, neopentyl, n-hexyl, 4-methylpentyl, n-octyl, phenyl and benzyl.
8. Complex according to any of claims 1 to 4 wherein R^6 is a group having the formula $-NR^{29}R^{30}$ and R^7 is a group having the formula $-NR^{31}R^{32}$, wherein R^{29} to R^{32} are independently selected from hydrogen, halogen, hydrocarbyl, substituted

hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more of R^1 to R^4 , R^6 and R^{29} to R^{32} are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents.

- 5 9. Complex according to any preceding claim wherein X is selected from halide, sulphate, nitrate, thiolate, thiocarboxylate, BF_4^- , PF_6^- , hydride, hydrocarbyloxy, carboxylate, hydrocarbyl, substituted hydrocarbyl and heterohydrocarbyl, and β -diketonates.
- 10 10. Complex according to claim 9 wherein X is selected from chloride, bromide, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl, methoxide, ethoxide, isopropoxide, tosylate, triflate, formate, acetate, phenoxide and benzoate.
11. Complex according to any preceding claim wherein B is selected from: β -diketonate, β -diketiminate, dithioacetylacetonate, carboxylate, carbamate, thiocarboxylate, dithiocarboxylate, thiocarbamate, dithiocarbamate, xanthate,
- 15 thioxanthate, phosphinate, thiophosphinate, dithiophosphinate, dialkyldithiophosphate, amidinate, bisimidazolate, phosphate, sulphurdiiminate, amidate, tropolonate, oxalate, oxalate ester, nitrate, nitrite, carbonate, squarate, croconate, sulphinate, sulphate, sulphite, fluorosulphate, hydroxamate, thiohydroxamate, and dithiohydroxamate, preferably optionally substituted acetylacetonates.
- 20 12. Complex according to any preceding claim wherein L is selected from primary, secondary and tertiary amines, amides, phosphoramides, phosphines, phosphites, ethers, thioethers, nitriles, carbonyl compounds, for example, esters, ketones, aldehydes, carbon monoxide, carbon dioxide, sulphoxides, sulphones and boroxines.
13. Complex according to any preceding claim wherein D is selected from BF_4^- , SbF_6^- , PF_6^- and tetrakis(aryl)borates.
- 25 14. Complex according to any preceding claim wherein M is Fe, Co or V.
15. Complex according to any preceding claim which is
 - 2,6-diacetylpyridinebis(2,6-diisopropylanil)Fe(acetylacetonate) $^+$ SbF_6^-
 - 2,6-diacetylpyridinebis(2-tert.-butylanil)Fe(acetylacetonate) $^+$ SbF_6^-
 - 30 2,6-diacetylpyridinebis(2,3-dimethylanil)Fe(acetylacetonate) $^+$ SbF_6^-
 - 2,6-diacetylpyridinebis(2-methylanil)Fe(acetylacetonate) $^+$ SbF_6^-

- 2,6-diacetylpyridinebis(2,4-dimethylanil)Fe(acetylacetonate)⁺ SbF₆⁻
 2,6-diacetylpyridinebis(2,6-dimethylanil)Fe(acetylacetonate)⁺ SbF₆⁻
 2,6-diacetylpyridinebis(2,4,6 trimethyl anil)Fe(acetylacetonate)⁺ SbF₆⁻
 2,6-dialdiminepyridinebis(2,6-dimethylanil)Fe(acetylacetonate)⁺ SbF₆⁻
 5 2,6-dialdiminepyridinebis(1-naphthil)Fe(acetylacetonate)⁺ SbF₆⁻ and
 2,6-bis(1,1-diphenylhydrazone)pyridine.Fe(acetylacetonate)⁺ SbF₆⁻
 2,6-diacetylpyridine(2,6-diisopropylanil)Co(acetylacetonate)⁺ SbF₆⁻
 2,6-diacetylpyridinebis(2,6-diisopropylanil)Fe(hexafluoroacetylacetonate)⁺ SbF₆⁻
 2,6-diacetylpyridinebis(2,4,6 trimethyl anil)Fe(hexafluoroacetylacetonate)⁺ SbF₆⁻
 10 2,6-diacetylpyridinebis(2-methylanil)Fe(hexafluoroacetylacetonate)⁺ SbF₆⁻
 2,6-diacetylpyridine(2,6-diisopropylanil)Co(hexafluoroacetylacetonate)⁺ SbF₆⁻
 2,6-diacetylpyridinebis(2,6-diisopropylanil)Fe(acetylacetonate)⁺ B(C₆F₅)₄⁻
 2,6-diacetylpyridinebis(2,4,6 trimethyl anil)Fe(acetylacetonate)⁺ B(C₆F₅)₄⁻
 2,6-diacetylpyridinebis(2-methylanil)Fe(acetylacetonate)⁺ B(C₆F₅)₄⁻
 15 2,6-diacetylpyridine(2,6-diisopropylanil)Co(acetylacetonate)⁺ B(C₆F₅)₄⁻
 2,6-diacetylpyridinebis(2,6-diisopropylanil)Fe(hexafluoroacetylacetonate)⁺
 (C₆F₅)₄⁻
 2,6-diacetylpyridinebis(2,4,6 trimethyl anil)Fe(hexafluoroacetylacetonate)⁺
 B(C₆F₅)₄⁻
 20 2,6-diacetylpyridinebis(2-methylanil)Fe(hexafluoroacetylacetonate)⁺ B(C₆F₅)₄⁻
 or
 2,6-diacetylpyridine(2,6-diisopropylanil)Co(hexafluoroacetylacetonate)⁺
 B(C₆F₅)₄⁻.
16. Polymerisation catalyst comprising
- 25 (1) a complex as defined in any preceding claim, and
 (2) an activating quantity of at least one activator compound.
17. Catalyst according to claim 16 wherein the activator is selected from
 organoaluminium compounds, hydrocarbylboron compounds and salts of a cationic
 oxidising agent and a non-coordinating compatible anion.
- 30 18. Catalyst according to claim 17 wherein the activator is selected from
 trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA), tri-
 n-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride,

dimethylaluminium chloride, diethylaluminium chloride, ethylaluminiumsesquichloride, methylaluminiumsesquichloride, and alumoxanes.

19. Catalyst according to any one of claims 16 to 18, further comprising a neutral Lewis base.

5 20. Catalyst according to claim 19 wherein the neutral Lewis base is selected from alkenes (other than 1-olefins) or alkynes, primary, secondary and tertiary amines, amides, phosphoramides, phosphines, phosphites, ethers, thioethers, nitriles, esters, ketones, aldehydes, carbon monoxide and carbon dioxide, sulphoxides, sulphones and boroxines.

10 21. Catalyst according to any one of claims 16 to 20 which is supported on a support material comprising silica, alumina, $MgCl_2$ or zirconia, or on a polymer or prepolymer comprising polyethylene, polypropylene, polystyrene, or poly(aminostyrene).

22. Catalyst according to any one of claims 16 to 21 which comprises more than one complex as defined in any of claims 1 to 15, or a complex as defined in any of claims 1 to 15 plus a tridentate nitrogen-containing Fe or Co complex, which is preferably 6-
15 diacetylpyridinebis(2,4,6-trimethyl anil) $FeCl_2$.

23. Catalyst according to any one of claims 16 to 21 which comprises a complex as defined in any of claims 1 to 15 plus a further catalyst suitable for the polymerisation of 1-olefins, preferably a Ziegler-Natta catalyst system, metallocene-based catalyst, monocyclopentadienyl- or constrained geometry based catalyst, or heat activated
20 supported chromium oxide catalyst (eg Phillips-type catalyst).

24. Process for the polymerisation or copolymerisation of 1-olefins, comprising contacting a monomeric olefin under polymerisation conditions with a complex or catalyst as defined in any preceding claim.

25. Process according to claim 24 comprising the steps of :

25 a) preparing a prepolymer-based catalyst by contacting one or more 1-olefins with a catalyst, and

b) contacting the prepolymer-based catalyst with one or more 1-olefins, wherein the catalyst is as defined in any of claims 16 to 23.

26. Process according to claim 24 or 25 wherein the polymerisation is conducted in the presence of hydrogen as a molecular weight modifier.
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27. Process according to any one of claims 24 to 25 wherein the polymerisation conditions are solution phase, slurry phase or gas phase.

28. Process according to claim 27 wherein the polymerisation is conducted under gas phase fluidised bed conditions.
29. Process according to claim 27 wherein the polymerisation is conducted in slurry phase in an autoclave or continuous loop reactor.
- 5 30. Process according to any one of claims 24 to 29 wherein the copolymerisation comprises formation of an ethylene/1-olefin/diene terpolymer in which the diene is preferably 1,4 pentadiene, 1,5-hexadiene, cyclopentadiene or ethylene norbornadiene, and the other 1-olefin is preferably propylene.
- 10 31. Use of a complex as defined in any of claims 1 to 15 as a catalyst for the polymerisation of 1-olefins.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/01385

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F15/00 C07F15/02 C07F15/06 C07F13/00 C07F9/00
C07F7/00 C08F10/00 C08F4/64 C08F4/68 C08F4/695
C08F4/70

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

1 August 2000

Date of mailing of the international search report

08/08/2000

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 00/01385

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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